

Nanocomposites of new biodegradable polyesters and polyesteramides

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Polymers are easily prepared by bulk polycondensation based on metal-halide salt formation, while crystallization is strongly influenced by incorporation and distribution of silicate nanoparticles.

Much effort currently focuses on biodegradable-polymer development for speciality use, such as in biomedicine and commodities. In general, biodegradable polymers are classified according to their origin. Synthetic polymers include aliphatic polyesters that contain nonaromatic carbon compounds, such as poly(L-lactide), poly(ϵ -caprolactone), poly(*p*-dioxanone), and poly(butylene succinate). Polyesters, produced by micro-organisms, are primarily polyhydroxyalkanoates. Polymers derived from natural resources include starch, cellulose, chitin, chitosan, lignin, and proteins.

Three suitable strategies for optimally combining material properties include newly designed polymer synthesis, use of natural monomers, and chemical modification of conventional polymers. Despite large investment in biodegradable polymers, they are still far from ideal substitutes for conventional commodity materials, since they are usually costly and possess disadvantageous physical properties. Therefore, it seems necessary to modify their chemical nature and/or enhance their performance through nanotechnology. Regarding the former, amide-group incorporation into a polyester chain is interesting, since polyesteramides should maintain degradability and establish strong intermolecular hydrogen-bonding interactions.¹⁻⁴ As for the latter, nanoparticles can be incorporated into the polymer matrix. Either approach may yield enhanced properties.

We report a synthetic method (see Figure 1) for preparing new polyesters and polyesteramides with an alternating sequence of glycolic acid and ω -hydroxyacid or ω -amino acid units.⁵⁻⁸ This avoids multiple selective protection and deprotection reaction steps. Polycondensation results in metal-halide salt formation, which becomes the driving force underlying the bulk reaction. The inorganic salt byproduct

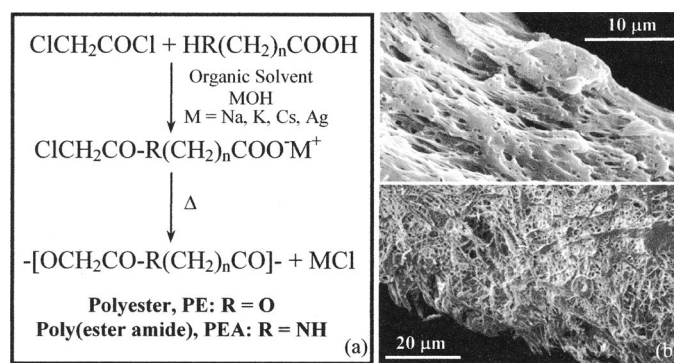


Figure 1. (a) Polyester (PE) and polyesteramide (PEA) synthesis by bulk polycondensation and metal-halide salt formation from chloroacetate derivatives of an ω -amino acid or ω -hydroxyacid. (b) Top: Typical porous matrix obtained after metal-halide salt removal. Bottom: Scaffold prepared from electrospun polyester microfibers. C: Carbon. Cs: Cesium. Cl: Chlorine. H: Hydrogen. N: Nitrogen. O: Oxygen. K: Potassium. Ag: Silver. Na: Sodium. Δ : Heat. *n* is an integer.

is easily removed by washing the sample with water, and we obtain porous textures of potential biomedical-technology interest. New polymers can be electrospun into micro/nanofibers to produce scaffolds useful for tissue engineering (see Figure 1).

We demonstrate that nanocomposites with exfoliated or intercalated structures can be prepared by in situ polymerization of the corresponding monomer salts (such as sodium *N*-chloroacetylaminohexanoate) and an organo-modified montmorillonite (such as Cloisites 25A, 20A, or 30B).⁹ We further find that polymerization kinetics under both nonisothermal and isothermal conditions appear strongly influenced by the presence of organo-modified montmorillonite. We employ IR spectroscopy and wide-angle x-ray diffraction to study the polymerization process, for example, the time evolution of characteristic metal-halide

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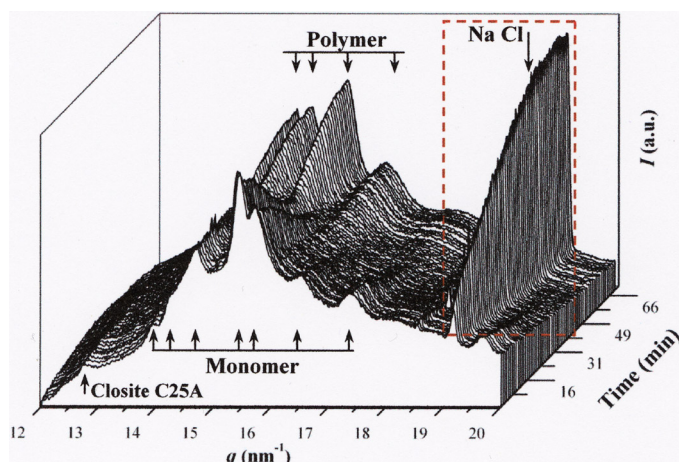


Figure 2. X-ray-diffraction profiles taken during nonisothermal polymerization, performed at a heating rate of 20°C/min, with a mixture of Cloisite 25A (C25A, 3% by weight) and the monomer comprised of glycolic acid and 6-aminohexanoic acid units. Arrows indicate typical reflections of C25A, monomer, polymer, and sodium chloride (NaCl). q : Scattering angle. I : Intensity in arbitrary units (a.u.).

reflection-diffraction intensity (see Figure 2). Results indicate a critical influence of clay particles on chain mobility and the frequency at which reactive groups are close enough to facilitate the condensation reaction. Furthermore, activation energy decreases relative to that found for the neat monomer, when in situ polymerization renders an intercalated structure. Nanoconfinement in the silicate galleries may favor polycondensation reactions.

Silicate-particle arrangement in the polymer matrix strongly depends on the nature of the polymer, organo-modifier compound, and preparation method (such as in situ polymerization, solution-intercalation film casting, and melt mixing). We prepared nanocomposites with different structures to gain insight into the influence of clay distribution on crystallization processes. Final structures were always determined by following the disappearance or shift toward a higher spacing of the layered silicate basal reflection or by thin-section morphological observations (see Figure 3).

Optical microscopy studies indicate that polymer primary nucleation density is enhanced by clay-particle incorporation in both hot and cold crystallization experiments, when an intercalated structure is obtained. Thus, silicate particles act as effective nucleating agents at low degrees of compatibility. This contrasts with our observations of practically exfoliated structures (such as when organo-modified clay is highly miscible with the polymer matrix), which indicate a decrease in primary nucleation (see Figure 4). The degree of crystallinity is always slightly lower for nanocomposite samples, suggesting a disturbing effect of the

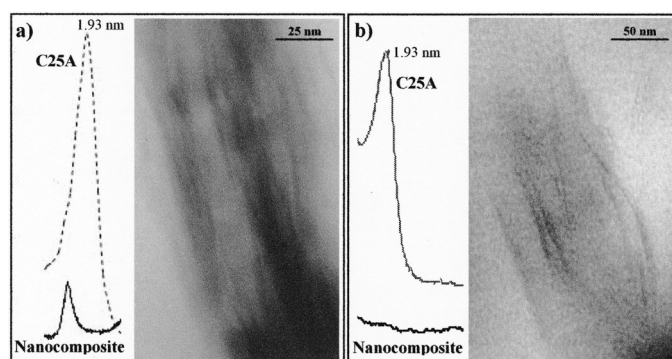


Figure 3. X-ray-diffraction profiles and electron micrographs corresponding to nanocomposites with an (a) intercalated or (b) exfoliated structure, prepared from Cloisite 25A and the PEA comprised of glycolic acid and 6-aminohexanoic acid units.

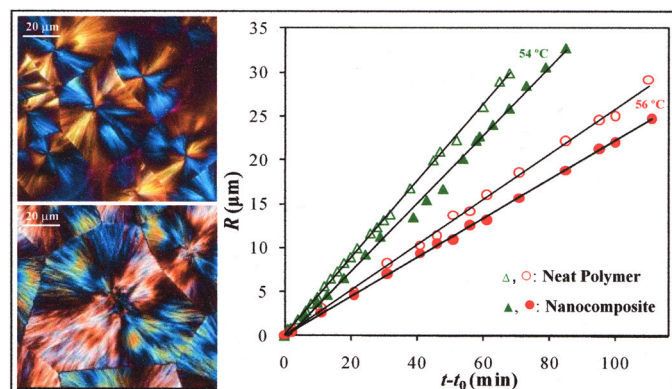


Figure 4. Spherulitic morphologies, obtained by isothermal crystallization at 54°C, of (top) the PE comprised of glycolic acid and 6-hydroxyhexanoic acid units, and (bottom) its nanocomposite with C25A, which possesses an exfoliated structure. Differences in morphology and nucleation density, as well as a decrease in growth rate (right) with nanoparticle addition, are evident. R : Spherulite radius. t : Time.

clay particles on crystallization, which may also impact final spherulitic textures (for example, fibrillar or ringed). In all cases, clay-particle addition slightly reduces radial growth rate (see Figure 4), since both secondary nucleation and molecular transport appear to be influenced by the presence of nanoparticles.^{9–12}

We performed small-angle x-ray-scattering analysis of cold and hot crystallization with neat samples and their nanocomposites. A focus was the normalized one-dimensional correlation function.^{11,12}

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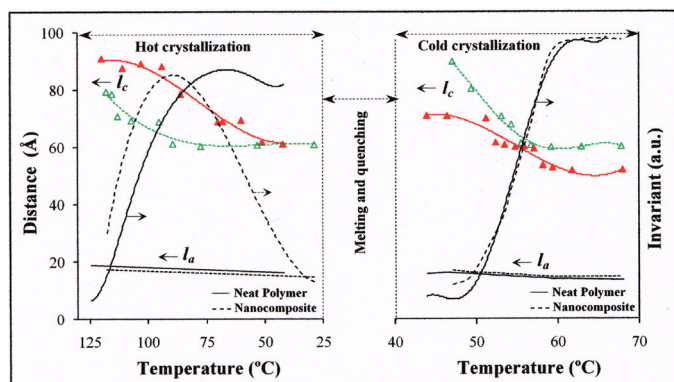


Figure 5. Temperature evolution of primary morphological parameters and the invariant during nonisothermal cold and hot crystallization ($3^{\circ}\text{C}/\text{min}$) of the neat PEA, comprised of glycolic acid and 6-hydroxyhexanoic acid units, and its intercalated nanocomposite with C25A (3% by weight). l_c : Crystalline lamellar thickness. l_a : Amorphous thickness.

We interrogated morphological features, such as crystalline, lamellar, and amorphous thicknesses, together with the scattering invariant. We found that amorphous thickness always remains essentially constant, while crystalline lamellar thickness decreases during both crystallization processes (see Figure 5). This suggests a lamellar insertion mechanism, which appears more significant for the nanocomposite samples. Note that these samples feature the largest decrease during cold crystallization. It occurs at a higher temperature during hot crystallization.

Future work entails studies of nanocomposites derived from polymer matrices with a variable ester/amide ratio and methylene content. These samples will be synthesized by copolymerization of a ω -hydroxyacid and ω -amino acid.

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